One-way optoelectronic switching of photochromic molecules on gold

Dulic, Diana; van der Molen, S.J.; Kudernac, T.; Jonkman, H.T.; de Jong, Jacob; Bowden, T.N.; Esch, J. van; Feringa, B.L.; Wees, B.J. van

Published in:
Physical Review Letters

DOI:
10.1103/PhysRevLett.91.207402

Publication date:
2003

One-Way Optoelectronic Switching of Photochromic Molecules on Gold

Diana Dulić,[1] S. J. van der Molen,[1] T. Kudernac,[2] H. T. Jonkman,[3] J. J. D. de Jong,[2] T. N. Bowden,[2] J. van Esch,[2] B. L. Feringa,[2] and B. J. van Wees[1]

[1]*Physics of Nanodevices, Materials Science Centre, Nijenborgh 4, 9747 AG Groningen, The Netherlands*
[2]*Stratingh Institute for Chemistry and Technology, Materials Science Centre, Nijenborgh 4, 9747 AG Groningen, The Netherlands*
[3]*Molecular Materials and Devices, Materials Science Centre, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

(Received 16 June 2003; published 14 November 2003)

We investigate photochromic molecular switches that are self-assembled on gold. We use two experimental techniques; namely, the mechanically controllable break-junction technique to measure electronic transport, and UV/Vis spectroscopy to measure absorption. We observe switching of the molecules from the conducting to the insulating state when illuminated with visible light ($\lambda = 546$ nm), in spite of the gold surface plasmon absorption present around this wavelength. However, we fail to observe the reverse process which should occur upon illumination with UV light ($\lambda = 313$ nm). We attribute this to quenching of the excited state of the molecule in the open form by the presence of gold.

DOI: 10.1103/PhysRevLett.91.207402 PACS numbers: 78.67.Bf, 73.63.Rt, 85.65.+h

A great challenge to present-day applied science is developing electronic devices on the nanometer scale. It is especially the field of molecular electronics that offers great potential, since molecules can be developed that perform new operations unattainable by conventional semiconductor technology [1–5].

We study a special class of molecules, the so-called photochromic molecular switches, in particular, the dithienylcyclopentenes [6,7] (Fig. 1). They consist of conjugated units, connected by a switching element. By exposing the molecule to light of specific frequencies, the covalent bonds in the switching element rearrange, and the conjugation throughout the molecule can be turned on and off. Because of the change in quantum confinement, the energy levels of the molecules will also be modified, resulting in a change in the absorption spectrum (and color) of the molecule. This explains the adjective photochromic. Implementation of this type of molecule in an electronic device would not only miniaturize it, but also add a completely new functionality to it. However, when a small entity such as a molecule is attached to macroscopic surroundings, it is not *a priori* clear that its functionalities are conserved. In this Letter we report that transport in our photochromic molecules can be switched from on to off. However, the reverse process does not take place, which we attribute to the influence of the gold attached to the molecules. A 1,2-bis[5′-(5″-acetylsulfanylthien-2″-yl)-2′-methylthien-3′-yl] cyclopentene photochromic switch has been especially designed for our electronic transport experiments. It consists of a central switching unit, two thiophene rings on both sides of the switching unit, and two thiol groups, protected with acetyl groups, at the ends of the molecule. In Fig. 1 we show the molecule in the closed state connected to two gold electrodes [form (a)]. In this situation conduction through the molecule occurs via an alternation of single-double carbon bonds, which extends throughout the whole molecule. By exposing the molecule to light of wavelength λ in the range 500 nm $< \lambda <$ 700 nm, the molecule will switch from form (a) to form (b). Form (b) is the open form of the molecule; the alternation of the single-double bonds is broken on the central ring, and the molecule is insulating. The length of the molecule is 1.74 nm in the closed form, and 1.81 nm in the open form. Details of the synthesis will be published elsewhere [8].

In order to measure single molecule transport we use the mechanically controllable break-junction (MCBJ) technique [9–11]. A layout of the technique is displayed in Fig. 2. By electron beam lithography we pattern the device on an elastic phosphor bronze substrate covered with an thin insulating layer of polyimide. The device is made of gold and has a narrow neck in the middle (see Fig. 2). After the gold deposition the polyimide below the

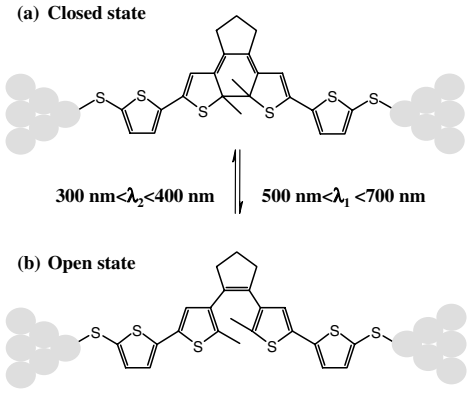

FIG. 1. Photochromic molecular switch between two Au contacts in closed state (a) and open state (b). By exposing the molecule to light of wavelength in the range 500 nm $< \lambda_1 <$ 700 nm, the molecule will switch from (a) to (b). In solution the protected molecule can be switched back to the (a) state by exposing it to UV light with wavelength in the range 300 nm $< \lambda_2 <$ 400 nm. However, this is not possible if the molecules are connected to gold.

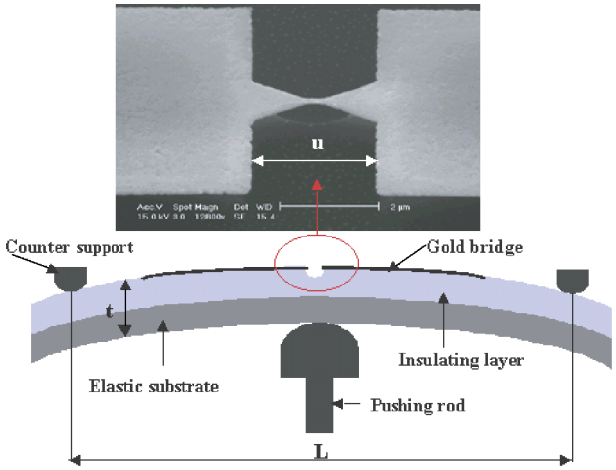

FIG. 2 (color online). Mechanically controllable break-junction (MCBJ) technique. Top: Scanning electron micrograph of the free standing gold bridge. Bottom: Layout of the technique (not to scale). The whole device is 2×2 mm^2. In reality the polyimide insulating layer is $\sim$1000 times thinner than the phosphor bronze.

bridge is etched away, leaving behind a freestanding gold bridge. We break the bridge by bending it with a three-point bending mechanism. We obtain a mechanical "attenuation factor" [11] $r = 6tu/L^2 = 1.7 \times 10^{-5}$, for our device, where $t = 0.42$ mm is the substrate thickness, $u = 2.4$ μm the suspended length of the bridge, and $L = 18.8$ mm the distance between the counter supports. This provides control of the spacing between the electrodes with a precision of 10 pm. The two open ends form point contacts to which the molecules will be attached via the thiol groups that form a strong chemical bond with gold. Prior to the experiments with the molecules we calibrated a number of devices in ambient and argon surrounding. We obtain an exponential increase of the resistance upon increase of the distance between the electrodes which is characteristic of the tunneling regime for the metal-air-metal junction. We can use our $R(d)$ data, where we take the distance d from the geometrical formula, to obtain an average value of the work function of gold $\langle\varphi\rangle = 6 \pm 2$ eV. This is in reasonable agreement with the experimental work function for gold which is 5.3 eV. Furthermore, we measure IV characteristics which can be satisfactorily fitted to the Simmons [12] and Stratton [13] formulas.

For our transport experiments, the molecular switches (in the open state) are dissolved in tetrahydrofuran (THF) solvent. By irradiation with UV light ($\lambda = 313$ nm) they are switched to the closed form. To prevent the molecules from switching back, all further experiments are performed in the dark. A droplet of solution is introduced onto the break junction with a microsyringe. Once the molecules reach the gold, the protective acetyl groups split off and an incomplete self-assembled monolayer (SAM) is formed [14]. In principle there are two approaches to achieve a molecular bridge. The first one is to break the junction, open the electrodes far apart, and then form a SAM [10]. In this situation the system is in the tunneling regime and the resistance has again an exponential dependence on the distance between the electrodes. Now we decrease the distance, applying a bias voltage of $V = 1$ V to assist a molecule to align between the electrodes, until we observe stable behavior. In our case this always happens at resistances of the order of MΩ, and it corresponds to the establishment of a Au-molecule-Au bridge [10]. The second approach is to first apply the solution and then open the wetted junction to form a molecular bridge [9]. We have tried both methods and obtain the same results.

Once the resistance is stabilized by molecular bridge formation, we measure IV characteristics; see Fig. 3(a). Our room temperature IV's do not show sharp features (see also Reichert *et al.* [10] and Heurich *et al.* [15]). After waiting for about half an hour we start illuminating the junction with the $\lambda = 546$ nm light, while monitoring the resistance as a function of time. In Fig. 3(b) we show a typical result. After a short time we observe a sharp increase in the resistance, which we attribute to switching of the molecule. The resistances we find after switching are in the GΩ range, about 3 orders of magnitude larger than the initial value. Such a ratio between the resistances of the open and closed form is in reasonable agreement with the work by Fraysse *et al.* [16], who both calculated and measured the coupling through the switching unit in a similar molecule. Furthermore it is consistent with recent calculations by Joachim who predicts a ratio of

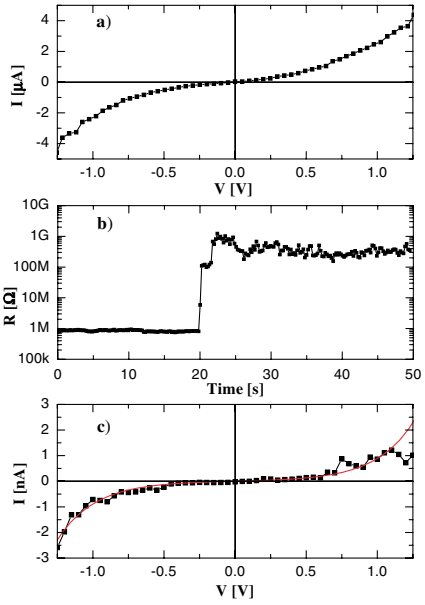

FIG. 3 (color online). MCBJ results. (a) Typical IV of the connected molecule in the closed form and (b) resistance versus time. At $t = 0$ a lamp is turned on ($\lambda = 546$ nm). After approximately 20 s a clear jump is observed (1 V bias). (c) Typical IV of the molecule after switching. The line is a fit to the Stratton formula (for details see text).

approximately 2 orders of magnitude [17]. In Fig. 3(c) we display a typical IV curve obtained after switching. Also shown is a fit to Stratton's tunneling formula $I = I_0 \sinh(eVd\sqrt{m/2\hbar^2\varphi})$ in which we put I_0 and φ as free parameters (m is the electron mass [18]). For d we use the calculated length of the open molecule (1.81 nm). From the fit we find $\varphi = 1.5$ eV and $I_0 = 4 \times 10^{-11}$ A.

We observed the switching process ten times out of 12 attempts. The two times that were not successful a much lower concentration of the molecules in THF (0.15 mM) was used. In the other ten experiments we used a concentration of 1 to 2 mM. Switching times ranging from 10 s to 6 min were observed [19]. After switching to the open state we attempted to switch the molecule back to the closed state by illuminating it with UV light (313 nm). This did not turn out to be possible. Since in solution the switching process from open to closed has a very high quantum yield (higher than from closed to open [20]) the absence of the reverse process seems to be related to the influence of the gold electrodes on the molecular system (see below).

One also has to consider other possibilities for a sharp jump in the resistance, such as migration of gold atoms or breaking of the gold thiol bonds. In order to exclude these possibilities we perform additional experiments: (a) illumination of the open junction without molecules and (b) illumination of molecular bridges formed by conjugated $T3$ molecules (three thiophene rings with two thiol end groups) [9]. In these experiments we do not observe such jumps in the resistance after the lamp was turned on (for at least 1 h).

In order to elucidate the results of the transport experiment, we study the influence of gold on the switching properties of the molecules in an independent experiment. For this, we measure UV/Vis absorption spectra of monothiol photochromic molecules [21] which were self-assembled on gold colloids (2–10 nm) suspended in toluene. The procedure for making the SAM on gold colloids will be published elsewhere [8].

For comparison we first show the absorption spectra of the molecules in the solution *without* gold in Fig. 4(a). The broad absorption peak around $\lambda = 550$ nm is characteristic for the closed switch (switching to the open state). Upon irradiating the solution with light of $\lambda = 546$ nm it vanishes completely (indicating a complete conversion to the open form), but it reappears by illuminating with $\lambda = 313$ nm. In Fig. 4(b) we show spectra of switches in the closed form self-assembled on gold before and after one day of illumination ($\lambda = 546$ nm). The characteristic absorption peak is initially present, but it vanishes with time. The background absorption present in Figs. 4(b) and 4(c) is characteristic for gold colloids [22]. We perform a similar experiment with the open switch self-assembled on gold colloids. Even after two days of irradiation with $\lambda = 313$ nm, there is no change in the spectrum [see Fig. 4(c)]. This confirms our MBCJ result that there is no switching back once the molecules are connected to

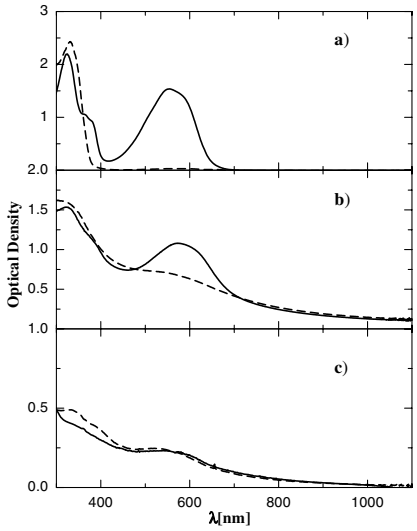

FIG. 4. Absorption spectra of the molecular switches. (a) Molecular switches in toluene. Solid line: closed form; dashed line: open form. The switching process in solution shows excellent reversibility. The decay half time for opening is a few minutes [8]. (b) Closed form self-assembled on gold colloids. Solid line: before irradiation with $\lambda = 546$ nm; dashed line: after one day of irradiation. From the curves taken in between we get a decay half-time of 40 min. (c) Open form self-assembled on gold. Solid line: before irradiation with $\lambda = 313$ nm; dashed line: after two days of irradiation. Since the optical density is proportional to concentration, the absolute values of the y axes in (b) and (c) are different.

gold. We attribute the small shoulder around 520 nm in Fig. 4(c) and in the final curve of Fig. 4(b) to the gold surface plasmon absorption [22]. Interestingly the surface plasmon absorption does not prevent the molecule from switching to the open form, although it does decrease the efficiency of the process.

To provide understanding for our findings, we investigate the switching process theoretically and discuss qualitatively the influence of gold on it. For this, potential curves were calculated using a selection of semiempirical quantum chemical computational methods implemented in the HYPERCHEM 6.0 program package (provided by Hypercube, Inc). The ground state potential curve was generated in a procedure in which the switching coordinate q (the distance between the carbon atoms which are responsible for the ring closure process) was changed in a systematic way between 0.13 and 0.4 nm. The total energy was calculated with the AM1 quantum chemical semiempirical method. For each q, the geometry of the molecule was fully optimized using a conjugate gradient procedure (Polak-Ribiere). We calculate the singlet excited state manifold with the Zerner intermediate neglect of differential overlap/spectroscopy method in which we incorporate ten occupied and ten unoccupied orbitals in the single excited state configuration interaction procedure. In Fig. 5 we plot, as a function of q, the ground state energy of the molecule with respect to the vacuum level

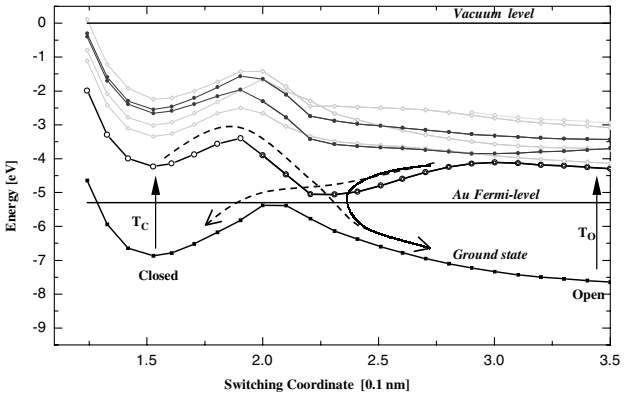

FIG. 5. Potential energy curves of the molecular switch along the switching coordinate q (black lines: optically allowed states; gray lines: optically forbidden excited states). The vacuum level is set at 0 eV. The switching process is initiated by an excitation to the first excited state (T_c, T_o). For a molecule in solution, the evolution of the switching process is indicated with dashed arrows. For a molecule connected to gold, however, the potential curve of the first excited state comes very close to the Au Fermi level (at $0.22 < q < 0.25$ nm), resulting in an efficient mixing of these respective states. When the open molecule goes to the first excited state (T_o), the closing process sets in, i.e., the excited state potential curve is followed towards lower q (solid arrow). However, when $0.22 < q < 0.25$ nm, the interaction with the gold makes the excited molecule relax back to the ground state (at the right side of the local maximum), and hence back to the open form. As a consequence there is no switching from the open to the closed form.

(the vacuum level is here defined as the total energy of the molecule with one electron removed; i.e., it is equal to the ionization potential of the molecule). Within the Koopmans theorem, this ionization potential is representative for the position of the highest occupied molecular orbital (HOMO) of the molecule. In the same approximation the energy of the electron addition state (electron affinity) is the energy of the lowest unoccupied molecular orbital (LUMO). In that description the optical and conduction gap coincide and the first excited state mimics the HOMO-LUMO gap. The ground state and excited state profiles shown here are very similar to the results obtained by Ern *et al.* [23] using a different method. In Fig. 5 we have drawn the paths for ring opening and closure for the *isolated* molecule upon optical excitation in the UV and visible spectral region. Clearly the ring opening process is expected to have a lower quantum yield than the reverse process, due to the presence of a barrier [20]. To consider the influence of gold on the molecular system, we have also plotted the Fermi level of polycrystalline gold (5.3 eV with respect to the vacuum level) in Fig. 5. We relate the failure of the closing process to the proximity of the gold Fermi level and the excited state molecular energy for $0.22 < q < 0.25$ nm. As a consequence, an efficient mixing of the gold states and the first excited molecular electronic state is expected, taking place at the right side of the ground state maximum. This results in quenching of the excited open state inhibiting the ring closure process. The electronic excited state involved in the ring opening process, on the other hand, is separated by more than 1 eV from the gold Fermi level. Hence, the ring opening process is not inhibited. Note that the foregoing considerations on the Koopmans theorem justify plotting molecular energy states and the gold Fermi level together.

In conclusion, we performed two complementary experiments to examine the influence of gold on the switching properties of photochromic molecular switches. Both sets of measurements show that for the molecule-gold system the switching occurs only in one direction, namely, from closed to open form. We attribute this to quenching of the first excited state of the open form of the molecule under the influence of gold.

We thank Marius Trouwborst, Bernard Wolfs, and Siemon Bakker for technical support. This work was financed by both FOM and NWO.

[1] A. Aviram and M. A. Ratner, Chem. Phys. Lett. **29**, 277 (1974).
[2] C. Joachim *et al.*, Nature (London) **408**, 541 (2000).
[3] J. C. Ellenbogen and J. C. Love, *Architectures for Molecular Electronic Computers* (IEEE, New York, 2000).
[4] J. Park *et al.*, Nature (London) **417**, 722 (2002); W. Liang *et al.*, Nature (London) **417**, 725 (2002).
[5] C. P. Collier *et al.*, Science **289**, 1172 (2000).
[6] M. Irie, J. Org. Chem. **53**, 803 (1988); M. Irie *et al.*, Nature (London) **420**, 759 (2002).
[7] B. L. Feringa, *Molecular Switches* (Wiley-VCH, Weinheim, Germany, 2001).
[8] T. Kudernac *et al.* (unpublished). See also L. N. Lukas, Ph.D. thesis, Rijksuniversiteit Groningen, 2001.
[9] C. Kergueris *et al.*, Phys. Rev. B, **59**, 12 505 (1999).
[10] J. Reichert *et al.*, Phys. Rev. Lett. **88**, 176804 (2002).
[11] J. M. van Ruitenbeek *et al.*, Rev. Sci. Instrum. **67**, 108 (1996).
[12] J. G. Simmons, J. Appl. Phys. **34**, 1793 (1963).
[13] R. Stratton, J. Phys. Chem. Solids **23**, 1177 (1962).
[14] J. M. Tour *et al.*, J. Am. Chem. Soc. **117**, 9529 (1995).
[15] J. Heurich *et al.*, Phys. Rev. Lett. **88**, 256803 (2002).
[16] S. Fraysse *et al.*, Eur. J. Inorg. Chem. **7**, 1581 (2000).
[17] C. Joachim (private communication).
[18] Here we assume the effective mass $m = 9.1 \times 10^{-31}$ kg, unlike W. Wang *et al.*, Phys. Rev. B **68**, 035416 (2003).
[19] The switching times were somewhat dependent on the lamp we used; a 300 W Xe lamp gives lower times than a 200 W Hg lamp.
[20] P. R. Hania *et al.*, J. Phys. Chem. A **106**, 8498 (2002).
[21] More precisely, we use a 1-[5′-(5″-acetylsulfanylthien-2″-yl)-2′-methylthien -3′-yl] -2-[5′-(5″-methylthien-2″-yl)-2′-methylthien -3′-yl] cyclopentene photochromic switch.
[22] U. Kreibig *et al.*, Z. Phys. D **12**, 505 (1989); M. J. Hostetler *et al.*, Langmuir **14**, 17 (1998).
[23] J. Ern *et al.*, J. Lumin. **87–89**, 742 (2000); J. Ern *et al.*, Chem. Phys. **246**, 115 (1999).